Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials

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ABSTRACT

A mixture of polyethylene (PE), polyethylene-terephtalate (PET), polypropylene (PP) and Nylon was submerged in marine water during 12 moths. The chlorine content of these plastics was measured through the passing time. Thermobalance was used to look for differences in the thermal decomposition of the plastics during in that time interval. Degradation of PET, PP and Nylon produced changes in the weight loss curve, but behaviour of PE is confusing. Pyrolysis and combustion at 850 ºC was finally performed to get knowledge of the possible differences in the emission of main gases, volatiles and semivolatiles including polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (ClBzs), polychlorinated phenols (ClPhs), polybrominated phenols (BrPhs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Results show that the emission of chlorinated species is somewhat not affected by the chlorine content of the plastics mix. The production of PCBs and PCDD/Fs was very low, under 4 pg WHO-TEQ/g.

Keywords: Plastics; PAHs; Dioxins; Marine water; Pyrolysis; Combustion

1. Introduction

The presence of marine debris is a cause for concern due to several reasons. These debris have been identified as harmful to organisms and to human health (Rochman et al., 2013); also these debris have the potential to increase the transport of organic and inorganic contaminants(Avio et al., 2017; Gaylor et al., 2012; Iñiguez et al., 2017; Rochman et al., 2013).

The material most commonly found in marine debris are glass, metal, paper and plastic (Cózar et al., 2014; OSPAR, 2007). The most commonly used plastics are polyethylene, polypropylene and polyethylene terephthalate, therefore, they are the most frequently found in the marine environment too (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Iñiguez et al., 2016; Ruiz-Orejón et al., 2016).

The annual input of plastics in the oceans increases every year. It is estimated that in 2015 around 9.1 million tons were accumulated (Jambeck et al., 2015).

One possible alternative for waste disposal is thermal decomposition through pyrolysis or combustion. These processes provide a reduction in waste volume and involve profitable energetic and/or chemical products. Nevertheless, the possible emission of pollutants during non-controlled plastic thermal degradation may create a serious hazard for human health and for the environment. In this way, it is important to control and reduce the emission of pollutants, and be aware of the chemical mechanisms involved in the thermal decomposition.

Different studies attempt to clarify the effects of chlorine content in waste on the formation mechanisms of polychlorinated pollutants, especially dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (Gullett et al., 2000; Sablier et al., 2010; Wang et al., 2003; Wyrzykowska et al., 2009). The study done in 2003 by Wang et al. showed differences in the emission when the chlorine level in the waste is higher than 0.8-1.1 %. If the level is lower than this threshold level, the formation of PCDDs dominates, probably because the chlorine is used to chlorinate the non-substituted phenol to produce chlorophenols, which are important precursors for PCDDs. In other cases, the PCDFs increase faster. Other authors (Gullett et al., 2000) pointed out a poor correlation between total chlorine in waste streams and formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) during waste combustion., because the active chlorine (Cl) species are strongly dependent upon combustion conditions. Nevertheless, Yasuhara et al. (Yasuhara et al., 2003) showed that the presence of NaCl during the combustion of newspapers increased more than 70 times the emission of PCDD/Fs. Accordingly, Ma et al. (Ma et al., 2010) revealed that the production of chlorinated compounds is affected both by organic and inorganic chlorine.

Regarding the environmental impacts, there are many studies that investigate the pollution associated with plastics combustion and/or pyrolysis (Devaraj et al., 2015; Font et al., 2011; Iñiguez et al., 2017; Poerschmann et al., 2015). However, there is no study investigating the effect of contacting marine water with plastic materials in the thermal decomposition of the wastes. Following this line, the aim of the present work is to study the changes that suffer plastic materials in contact with marine water, and the differences in the emission of pollutants comparing the pyrolysis and the combustion of materials before and after having passed

one year in contact with marine water. Also, the chlorine content and the thermal behaviour are monitored during this time.

2. Materials and methods

2.1. Materials

Four main plastics components usually found in marine litter were studied for thermal decomposition. In this way, PE, PP, PET and Nylon were studied. The plastic components were submerged in marine water, in a 100 L drum, during a total period of one year. During this time, different samples were taken to measure the chemical composition and thermal behavior. Specifically, samples were taken at 2, 7 and 12 months, and were compared to the plastics before the treatment.

2.2. Determination of ions and NCV

The Net Calorific Value (NCV) was determined using a calorimetric bomb AC-350 Leco Instruments, and the inorganic anions content of the sample was measured by ionic chromatography following EPA methods 5050 and 9056 (US EPA, 1994a, 2007b).

2.3. TG runs

Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in a mixture nitrogen:oxygen = 4:1 (20 % oxygen, simulating air composition) with a total flow rate of 100 mL min-1. Dynamic experiments were carried out at 20 K min-1, from room temperature up to 1173 K. For each run, 4 ± 0.3 mg of sample were used.

2.4. Pyrolysis and combustion runs

The emissions from the thermal decomposition of marine plastic were studied comparing the decomposition before and after having the plastic submerged in the sea water. In this sense, a mixture of the four plastics was prepared in equal proportions, since it was representative of marine litter (Iñiguez et al., 2017). The pyrolysis and the combustion of this mixture were compared before and after passing one year in the marine water drum. During the rest of article, these samples will be named “MIX_original” and “MIX_12months”.

Combustion and pyrolysis runs of MIX_original and MIX_12months were carried out in a moving tubular reactor, which consists in a quartz tube (10 mm internal diameter) where the material was introduced in three quartz boats (70 mm long each) along the tube. Once the process programmed temperature was reached (850 ºC in all runs) inside the horizontal furnace and with a constant flow of gas passing through, the boats were introduced in the furnace at constant speed using a horizontal actuator. This experimental system has been previously described in detail (Conesa et al., 2013). Synthetic air (combustion runs) or nitrogen (pyrolysis runs) was introduced in parallel to the sample, with a constant flow of 500 mL min^{-1} (measured at 1 atm and 20 ºC). The sample mass in each run was around 0.5 g. Before the decomposition runs, a control containing no sample was carried out using the same experimental conditions (blank). For the combustion runs, an oxygen

ratio equal to 0.5 was selected, defined as the fraction between the actual and the stoichiometric air flow rate necessary for a complete combustion (Conesa et al., 2009).

The reproducibility of this type of experiments has been tackled in our laboratory. A previous study (Garrido et al., 2016) confirmed a good reproducibility for all compounds analyzed in the emissions from combustion and pyrolysis runs of wastes using a similar laboratory scale horizontal reactor. The obtained standard deviations were small in comparison with the average values; only for some small average values, the standard deviations were somewhat greater, but with relative standard deviations around 5%.

The outlet gas stream of each run was sampled to analyze the following pollutants:

- Gases and volatile compounds were collected using Tedlar® bags (Restek, USA). CO_2 and CO were analyzed by gas chromatography with thermal conductivity detector (GC-TCD) (Agilent 7820). Light hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A).

- PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs were collected in a polyaromatic Amberlite® XAD-2 resin (Supelco, Bellefonte, USA) placed at the exit of the furnace during the whole experiment. The Tedlar® bag was located after the resin.

Internal standards were employed to calculate the concentration of PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs in the samples. Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) supplied the deuterated standards used for the analysis of the 16 priority PAHs and Wellington Laboratories (Ontario, Canada) supplied the ^{13}C-labeled standards for ClPhs, ClBzs, BrPhs and PCDD/Fs. All the internal standards were added to the resin.

Next, the resin was successively extracted with a mixture of dichloromethane/acetone (1:1 vol) and toluene by Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the US EPA method 3545A (US EPA, 2000). The extract was divided into two fractions: approximately 30 wt.% was used for the analysis of PAHs, ClPhs, ClBzs and BrPhs (US EPA, 2007a) and the remaining 70 wt.% was employed for the analysis of PCDD/Fs (US EPA, 1994b).

PAHs, ClPhs, ClBzs and BrPhs were analyzed by GC-MS (Agilent GC 6890N/Agilent MS 5976N, Agilent Technologies, USA) following the US EPA method 8270D (US EPA, 2007a) as reference. ClBzs, ClPhs and BrPhs were analyzed in the SIR mode and the identification of each isomer was performed comparing the primary/secondary ion area ratio with that obtained in the calibration with the labelled compounds. For the analysis of PCBs and PCDD/Fs, a cleanup step was performed using the Power Prep automated system (FMS, Inc., Boston, MA) with three different columns: multilayer silica, basic alumina and activated carbon. The purified extract was analyzed by HRGC/HRMS. Regarding the analyses of PCBs and PCDD/Fs, the recoveries obtained for the labelled standards were within the ranges established by the reference standards (US EPA, 1994b).

3. Results and discussion

3.1. Inorganic anions analysis and net calorific value (NCV).

Figure 1 shows the main results of the characterization of the plastic materials picked up at the different samplings. The main inorganic anions content and the NCV were measured in samples taken at 0 (original), 2, 7 and 12 months after introducing the plastics in the marine water.

As can be seen in the Figure, plastics are quickly impregnated with the ions present in the water. In this sense, chloride is mainly incorporated to the plastics, especially PE that increases very quickly its chlorine content. Along time, the chloride content continues increasing, except in the case of PE that shows a high content from very early stages.

Respecting to the NCV (represented as 'x' in the graph), is more or less constant for each sample, without being affected by the passage of time. As expected, NCV of PP and PE are much higher than those of PET or Nylon).

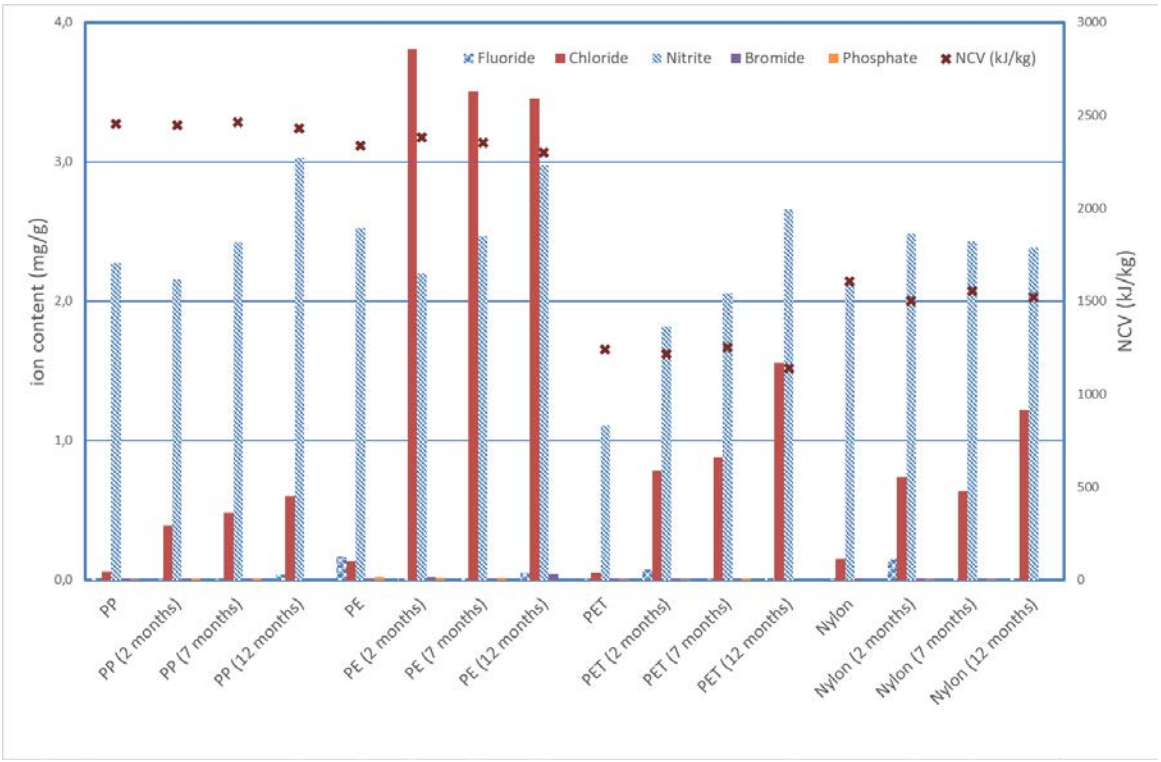

Figure 1. Evolution of inorganic anions content and NCV over time for samples submerged in marine water.

3.2. Thermogravimetric runs

Evolution of the thermal behavior of the plastic materials was followed by thermogravimetry. Samples were subjected to decomposition in the thermobalance at 20 K/min and were finally compared. As mentioned

before, synthetic air was used as carrier gas to test for the behavior of the samples in combustion conditions (Iñiguez et al., 2017). Measures were duplicated to test for the reproducibility that was very good.

Figure 2 shows the results for all plastic materials. As can be seen, all plastics were affected by the contact with the marine water. In general, thermal properties were affected, causing a weakening of the plastic over time. PET was the most affected sample, with Tmax (temperature were the decomposition rate is maximum) going from 446.3 ºC (Original PE) to 437.8 ºC (sample taken at 12 months). Nylon and PP also have an expected behavior as the degradation is easier as the polymer is submerged in the water.

In this way, PP was affected, but in this case the difference between the Tmax values was (373.0-351.3) ºC. PE behavior is confusing because it seems that the marine water environment produces a strengthening of the material, as the TG curves are moving to higher temperatures over the time. From the curves, Tmax are calculated at 0, 4, 7 and 12 months, being the values 416, 404, 407 and 418 ºC respectively. PE is also the polymer that more quickly increases its chlorine content, as stated before.

As can be seen in Figure SM1 of the supplementary material, the decomposition in inert atmosphere of four plastics was also studied in the thermobalance. Generally (Font et al., 2005) the presence of oxygen accelerates the decomposition, as it is the case of the materials studied in the present work.

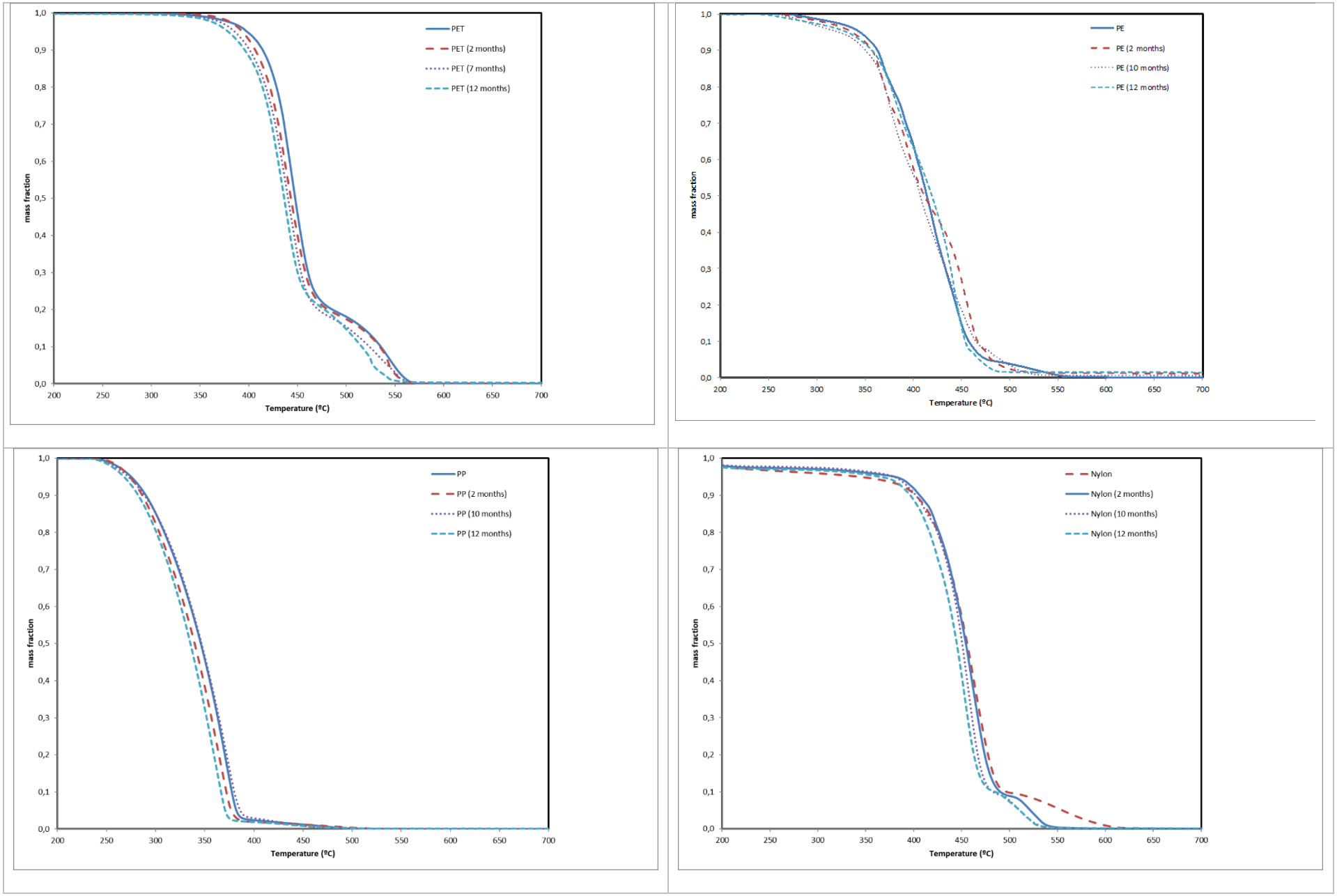

Figure 2. Thermal decomposition of the plastic materials at different time after being submerged in marine water.

3.3. Gases and volatile compounds emission during pyrolysis and combustion runs

As commented before, the sample MIX_12months was subjected to pyrolysis and combustion runs, and was compared to the MIX_Original decomposition. Figure 3 and Figure 4 show the evolution of the main gases produced in these runs. Ethylene and methane were the most abundant gases, especially in the pyrolytic conditions. The presence of oxygen in the combustion runs produces the oxidation of the gases and then the decrease of the main constituents, as it occurs with other materials (Conesa et al., 2009).

Comparing both samples, the differences are not important, in particular in the pyrolysis experiments. It could be because the Nitrogen content is very high in all samples. However, other authors suggested that the main factor affecting the emissions is the calculated oxygen ratio and not the flow rate used (Conesa and Domene, 2015). In this sense, it is consider this is not the reason for the small differences found.

Differences are shown in the combustion runs, where the production of methane, ethylene and isobutene is higher in the decomposition of the MIX_12months sample. In both processes, it is important to emphasize the high production of ethylene, which is expected taking into account the chemical structure of polyethylene. The CO and CO_2 yields obtained in the combustion runs were much higher than those detected in pyrolysis at 850 °C due to the fact that the increase of oxygen content in the atmosphere intensified the fuel combustion.

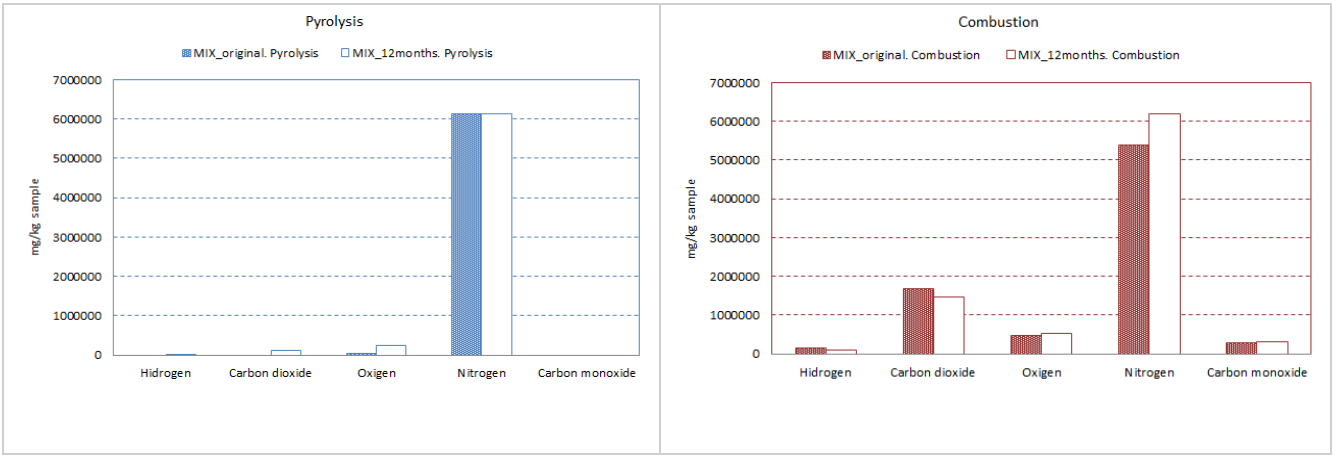

Figure 3. Gas emission during the pyrolysis and combustion of the plastics mixtures (GC-TCD).

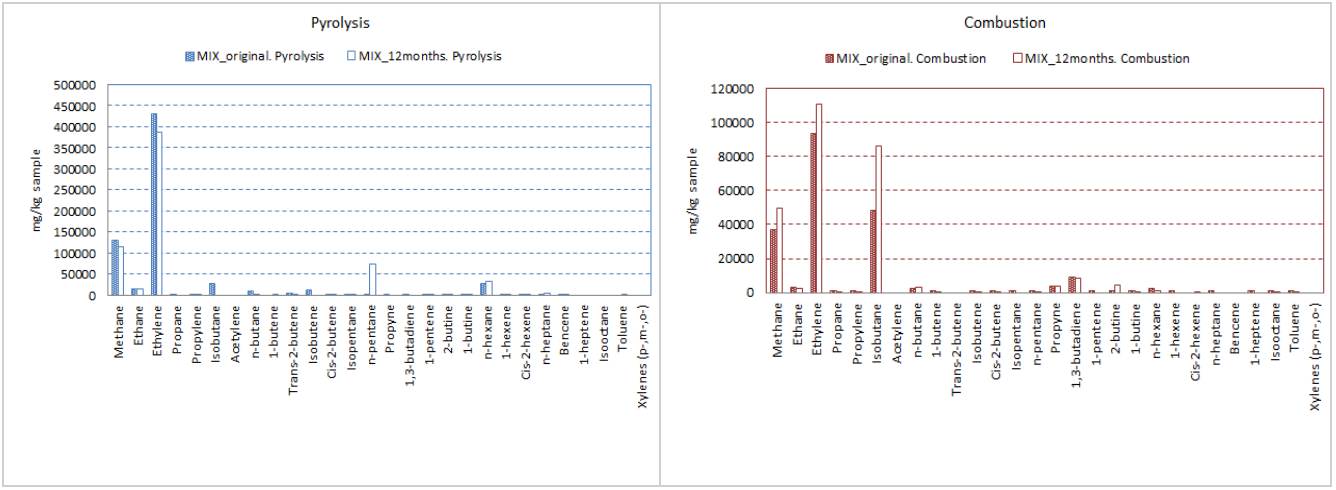

Figure 4. Gas emission during the pyrolysis and combustion of the plastic mixtures (GC-FID).

3.4. Semivolatile, PAHs and halogenated pollutants

Figure 5 shows the results for the emission of 16 priority PAHs in the pyrolysis and combustion runs. The emission of PAHs from both samples is almost the same. No differences were found.

On the other hand, the presence of oxygen affects in different ways the emission of PAHs, as expected (Rey et al., 2016). The emission of naphthalene decreased in the presence of oxygen, as expected since it is known that pyrolytic reactions are the primary source of PAH formation (Thomas and Wornat, 2008), being the naphthalene the mainly compound emitted in all cases. However, other PAHs like acenaphthylene and phenanthrene increased slightly in the combustion runs, but the difference is not significant. Remember that the combustion runs were done with an oxygen ratio of 0.5, i.e., in the presence of 50 % of the stoichiometric oxygen needed for the total combustion.

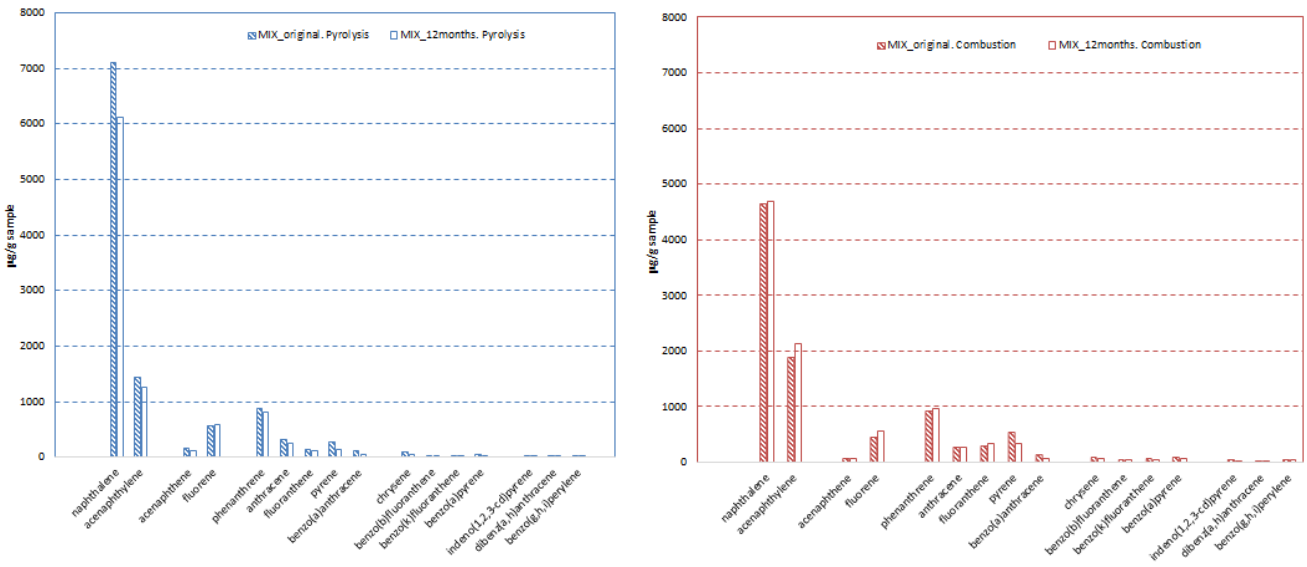

Figure 5. PAHs emission during the pyrolysis and combustion of the plastics mixtures.

Tables 1 to 3 presents the emission of chlorobenzenes (ClBz), chlorophenols (ClPh) and bromophenols (BrPh), respectively. The most abundant isomers of ClBz were di-ClBz with maximum values of ca. 200 µg/g sample. For all these pollutants, the emission was drastically decreased in the presence of oxygen.

The highest yields of ClBzs and ClPhs were observed in pyrolytic conditions; in such a way that the yields decreased with the presence of oxygen, consistent with the profile of PAHs. This tendency occurs also during the thermal decomposition of other wastes (Garrido et al., 2017; Rey et al., 2016). The maximum total yields are also similar lower than those detected with other wastes. In a previous work (Iñiguez et al., 2017) we determined that the content of ClBzs in plastics from marine environment was in the range 0.180–0.215 µg/g, being 1,2-dichlorobenzene the most abundant isomer in two different samples. In the present work, a maximum emission of ca. 208 µg/g is shown.

Respect to the effect on the emission of the contact with marine water, it is difficult to see a clear trend. From the data presented in Figure 1, an average value of chlorine content in the samples was calculated. Values of 0.10 mg/g and 1.70 mg/g can be assigned to MIX_Original and MIX_12months respectively. In general, emission levels of chlorinated pollutants are similar for both samples, indicating that the level of chlorine in the waste is not correlated with the emission of chlorinated species, at least in the ranges studied in this work.

On the other hand, the amount of BrPh evolved is almost nil in all runs performed, as it is the bromine content of the samples (Figure 1). A maximum value for the emission of total BrPh of 1.2 μg/g can be assigned. The formation of BrPhs was higher in pyrolytic conditions (1.2-1.0 μg/g) than in oxidative ones (0.4-0.7 μg/g). In pyrolysis process, the most abundant isomer in two both samples was 3,4-monobromophenol, being 3,4-dibromophenol the majority compound in the combustion runs. The minimum emission values for pyrolysis and combustion runs in all the samples were found in the isomer 2,4,5-tribromophenol.

Table 1. Chlorobenzenes emission from the pyrolysis and combustion of samples at 850 ºC.

	ClBz	μg/g sample			
		MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
Mono-	Mono-	2.065	3.495	1.907	1.102
Di-	1,3-	36.67	32.211	69.96	60.26
	1,4-	0.110	0.085	0.149	0.105
	1,2-	79.39	39.260	207.91	84.92
Tri-	1,3,5-	0.046	0.003	0.032	0.016
	1,2,4-	0.324	0.018	0.186	0.129
	1,2,3-	0.058	0.026	0.236	0.127
Tetra-	1,2,3,5-+1,2,4,5-	0.022	0.015	0.058	0.010
	1,2,3,4-	0.019	0.028	0.167	0.016
Penta-	Penta-	0.015	0.011	0.045	0.011
Hexa-	Hexa-	0.039	0.054	0.035	0.052

221 Table 2. Chlorophenols emission from the pyrolysis and combustion of samples at 850 ºC.

		µg/g sample			
	ClPh	MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
Mono-	2-	0.087	0.157	0.091	0.106
	3-+4-	99.91	61.21	245.48	413.48
Di-	2,4-	2.121	0.106	4.605	0.785
	2,5-	1.532	0.074	4.722	0.780
	2,3-	1.320	0.091	2.917	0.729
	2,6-	0.126	0.017	0.170	0.405
	3,5-	0.426	0.157	1.912	2.284
	3,4-	0.205	0.338	3.711	3.990
Tri-	2,3,5-	0.192	0.040	0.038	0.025
	2,4,6-	0.076	0.024	0.192	0.029
	2,4,5-	0.023	0.009	0.044	0.043
	2,3,4-	0.021	0.009	0.031	0.028
	2,3,6-	0.026	0.004	0.028	0.038
	3,4,5-	1.429	0.167	4.455	2.834
Tetra-	2,3,5,6-	0.084	0.041	0.074	0.090
	2,3,4,5-	0.095	0.018	0.066	0.077
	2,3,4,6-	0.053	0.033	0.014	0.007
Penta-	penta-	0.112	0.131	0.201	0.113

222 Table 3. Bromophenols emission from the pyrolysis and combustion of samples at 850 ºC.

		µg/g sample			
	BrPh	MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
MONO-	2-	0.041	0.019	0.151	0.149
	3-+4-	0.049	0.014	0.311	0.280
DI-	2,4-	0.021	0.013	0.099	0.046
	2,3-+2,5-	0.003	0.005	0.003	0.006
	2,6-	0.016	0.018	0.041	0.033
	3,5-	0.065	0.009	0.159	0.039
	3,4-	0.247	0.267	0.207	0.098
TRI-	2,3,5-	0.012	0.014	0.054	0.046
	2,4,6-	0.037	0.010	0.014	0.020
	2,3,4-	0.104	0.027	0.056	0.085
	2,4,5-	0.001	0.001	0.010	0.006
	2,3,6-	0.014	0.001	0.006	0.017
	3,4,5-	0.055	0.047	0.063	0.116
TETRA-	2,3,5,6-	0.052	0.019	0.012	0.069
	2,3,4,5-+2,3,4,6-	0.059	0.022	0.016	0.070
PENTA-	penta-	-	-	-	-

3.5. Polychlorobiphenyls (PCBs) and Dioxins/furans (PCDD/Fs)

Also PCBs and PCDD/Fs were measured in the decomposition runs. The emission levels of these pollutants were very low. Nonetheless, many of the samples presented undetectable amounts of some congeners. Tables SM1 and SM2 (Supplementary Material) show the amounts of the different PCB and PCDD/F congeners emitted, in pg WHO-TEQ/g sample, where a value of the limit of detection was assigned to the non-detects.

The total emission of PCDD/Fs was between 0.9 and 2.7 pg WHO-TEQ/g for all the runs, including pyrolysis and combustion runs of samples MIX_Original and MIX_12months. These values were quite lower than the emission measured in a similar experimental system for other materials, as is the case of sewage sludge (630 pg WHO-TEQ/g), used oils (80 pg WHO-TEQ/g) or PVC (4500 pg WHO-TEQ/g) and similar to that presented by meal wastes (12 pg WHO-TEQ/g), cotton textiles (8 pg WHO-TEQ/g) and polyester textiles (16 pg WHO-TEQ/g) (Conesa et al., 2009). Congener who most contributed to the total toxicity was 1,2,3,4-TCDD in all samples. Respect to the PCBs, a maximum emission level of 0.31 pg/g was detected. This is a very low amount and is not correlated to the level of chlorine in the samples, as is the case of PCDD/Fs.

4. Conclusions

In this work, a mixture of polyethylene, polyethylene-terephthalate, polypropylene and Nylon was submerged in marine water for 12 months. During this time, chlorine was mainly incorporated to the plastics, especially PE, that increased very quickly its chlorine content, reaching the highest value. The NCV of these polymers did not present significant variations over time.

In general, thermal properties of all plastics were affected by the contact with the marine water, causing a weakening of the plastic as time goes by. PET was the most affected polymer.

Pollutant emissions from thermal decomposition of this sample and the original were studied under inert and oxidizing atmosphere, being methane and ethylene the main compounds emitted in both cases. The yields of these gases were lower in the presence of oxygen.

Not differences were found in the emissions of PAHs from both samples (MIX_original and MIX_12 months), being the naphthalene the majority compound in all experiments. The highest yields of ClBzs and ClPhs were observed in pyrolytic conditions. The most abundant isomer in all samples was 1, 2-dichlorobenzene. On the other hand, both the bromine content in the samples and the amount of BrPhs evolved are almost nil in all the runs carried out. The emission levels of PCBs and PCDD/Fs were very low too.

In general, pollutant emissions are higher when the content of oxygen in the process is lower, that is, in pyrolytic conditions. Otherwise, results show only small differences between MIX_original and MIX_12months. So it can be said that the level of chlorine in the waste is not correlated with the emission of chlorinated species, at least in the ranges studied in this study.

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